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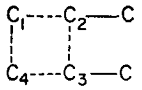
Four-Center Mechanism for Olefin Reactions

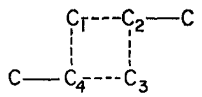
The occurrence of disproportionation, polymerization, and isomerization of olefins over similar catalysts or simultaneously over the same catalyst suggests a similarity of mechanisms for these reactions. However, this is not to say that one can predict a given catalyst will promote one or more of these reactions or that a given catalyst known to promote one of these reactions also will promote another. Reaction schemes involving a four-center, cyclobutane intermediate such as proposed by Schoepfle and Ryan (*1*) for the dimerization of diphenylethylene also have been postulated for the disproportionation of olefins (*2*) and the dimerization of propylene (*3*). This note discusses a mechanistic relationship of olefin reactions occurring via the four-center intermediate.

Olefins disproportionate over a number of heterogeneous catalysts such as hexacarbonyls and oxides of molybdenum and tungsten supported on alumina or silica (*4, 5, 6*). Bradshaw, Howman, and Turner (*2*) suggested a four-center or quasi-cyclobutane mechanism for this reaction. Isotope studies by Clark (*7*) and by Mol, Moulijn, and Boelhouwer (*8*) support the four-center mechanism for olefin disproportionation. Calderon and associates (*9*) arrived at this mechanism for olefin disproportionation from studies with soluble tungsten complexes as catalyst.

The four-center intermediates postulated with propylene are



(I)



(II)

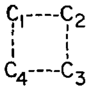
Dissociation of (I) by breaking of the opposite C_1–C_2 and C_3–C_4 ring bonds forms the observed disproportionation products, ethylene and 2-butene (*4*). Breaking of the other opposite pair of ring bonds in (I) or of either pair of opposite ring bonds in (II) results in the starting material. A hydrogen shift (intramolecular hydrogen transfer) between carbon atoms is not needed for disproportionation.

In our early disproportionation studies we contacted ethylene with a series of catalysts prepared by supporting Group VI

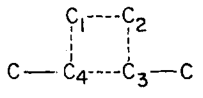
Catalyst: alumina impregnated with—	Products
$W(CO)_6$	21% Propylene, 71% 1-butene, 8% 2-butene
$Mo(CO)_6$	8% Cyclopropane, 12% methylcyclopropane, 28% propylene, 26% 1-butene, 26% 2-butene
$Cr(CO)_6$	3% Butenes, 97% solid polyethylene

hexacarbonyls on alumina and obtained different products with the different hexacarbonyls (*10*).

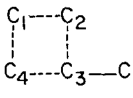
We think that 1-butene is obtained from ethylene by intermediate (III) in which breaking one bond and hydrogen shift occurs.



(III)



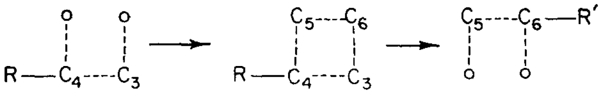
(IV)



(V)

2-Butene is produced by double-bond isomerization, and propylene is formed from ethylene and 2-butene by breaking ring bonds C_1–C_2 and C_3–C_4 of structure (IV). Some catalyst sites are apparently specific enough to close the cyclopropane ring and to cause a hydrogen shift in structures (IV) and (V) producing methylcyclopropane and cyclopropane. Adjacent bonds C_2–C_3 and C_3–C_4, structures (IV) and (V), are broken and new bond C_2–C_4 is formed. Breaking of ring bond C_1–C_2 of structure (III) and forming bond C_1–C_3 is a simpler route to methylcyclopropane; however, this scheme does not provide a direct path to cyclopropane.

Long-chain polyethylene is produced by the same mechanism postulated for 1-butene if the product remains on the catalyst and reacts repeatedly with ethylene by the following sequence. Bond C_2–C_3 of (III) breaks, forming (VI) which reacts with ethylene to form (VII). Bond C_4–C_5 then ruptures to give (VIII), etc.



(VI) (VII) (VIII)

In the polymerization of propylene to solid polymer by this mechanism, product with methyl branching on alternate chain carbons is obtained when propylene, or propylene and the intermediate product, forms structures of type (II).

Polymerization of olefins occurs over supported transition metal oxides and similar catalysts (*11*). Nickel oxide supported on silica-alumina is very active for dimerization of light olefins (*12, 13*). Recently Imai and co-workers (*3*) concluded that propylene dimerization over nickel oxide supported on silica-alumina proceeds by a cyclobutane intermediate instead of by the carbonium ion mechanism. They postulated structures (I) and (II) as intermediates for this reaction. Dissociation of (I) accompanied by a hydrogen shift and breakage of the C_2–C_3 bond gave *n*-hexane, of the C_1–C_2 bond (equivalent to C_3–C_4) gave 3-methylpentene, and of C_1–C_4 bond gave 2,3-dimethylbutene. Breakage of any one of the ring bonds of (II) accompanied by a hydrogen shift gave methylpentene. The authors claim that this mechanism alone accounts for the product distribution from polymerization of propylene and for the greater reactivity of ethylene than of the higher molecular weight olefins.

One difference between polymerization and disproportionation is that in polymerization a net hydrogen shift between carbon atoms must occur. There is no such shift in disproportionation. Thus, the relative rates of polymerization and disproportionation should be influenced by the ability of the catalyst to promote hydrogen shift. The relative rates also should be influenced by process conditions, but without knowledge of the rate-limiting steps and activation energies no *a priori* generalizations can be made. Isomer distribution of the polymerization product should depend upon the relative bond strengths in the complex and any directive preference for hydrogen shift between carbon atoms.

This four-center mechanism can be extended to cover skeletal isomerization of olefins with the exception of butene. The requirement for this is that the olefin coils into a cyclobutane structure on the catalyst site and hydrogen shift and bond rupture occur. Skeletal isomerization of *n*-butene, which is more difficult than that of *n*-pentene, cannot proceed by the four-center mechanism; a cyclopropane intermediate is needed for *n*-butene isomerization. Pines and Csicsery (*14*) have proposed cyclobutane-type and cyclopropane-type intermediates for the dehydroisomerization of hydrocarbons over "nonacidic" chromia-alumina. Okamoto and co-workers (*15*) have suggested four-member ring intermediates to account for the observed rearrangement of the carbon skeleton during the dehydrogenation of 1-butene-1-^{14}C to produce 1,3-butadiene over acidic chromia-alumina catalyst.

The mechanistic relationships of these catalytic olefin reactions can be summarized as follows:

(1) Disproportionation occurs when two molecules are adsorbed on the catalyst with the formation of a four-center complex and are then desorbed with the breaking of two opposite bonds without hydrogen shift.

(2) Polymerization occurs when two molecules are adsorbed with the formation of a four-center complex and are then desorbed with the breaking of one bond and hydrogen shift.

(3) Skeletal isomerization occurs when one molecule is adsorbed with the formation of a four-center complex and is then desorbed with the breaking of one bond and hydrogen shift.

(4) Another distinct reaction occurs when the four-center complex dissociates by rupture of adjacent ring bonds with hydrogen shift to form the cyclopropane ring.

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